

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Patent Application of

SCHNEIDER et al

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Serial No. 08/893,371

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Examiner: Hollinden

For: STABLE MICROBUBBLES SUSPENSIONS INJECTABLE
INTO LIVING ORGANISMS

* * * * *

Honorable Commissioner of Patents
and Trademarks
Washington, DC 20231

Sir:

DECLARATION OF MICHEL SCHNEIDER UNDER 37 CFR 1.132

I, MICHEL SCHNEIDER, a citizen of France, hereby declare and state as follows:

That I am an applicant and an inventor in respect of the above-identified application, I am familiar with the contents of that application and I am also familiar with U.S. patents 5,567,413 and 5,536,490 both to Klaveness et al.

That in the specification of the above-identified application the expression used in the first full paragraph of page 15 referring to innocuous physiologically acceptable gases as "CO₂, nitrogen, N₂O, methane, butane, freon, and mixtures thereof" refers to various physiologically acceptable gases forming the suspensions of microbubbles of the invention.

As of April 1990, one of ordinary skill in the art of chemistry would have understood that the word "freon" included fluorinated hydrocarbon gases and perfluorinated hydrocarbon gases,

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SCHNEIDER et al
Serial No. 08/893,371

such as perfluoromethane. The word "freon" originally was a DuPont trademark and therefore, one of ordinary skill in the art of chemistry would look to see how DuPont defined "freons" if that person were seeking a definition of that word. A DuPont Technical bulletin dated 1964, copy attached, defines "freons" as "organic compounds containing one to four carbon atoms and fluorine. Chlorine, bromine, and hydrogen atoms also may be present." Perfluorocarbons in which all of the hydrogen atoms attached to the carbon atoms are replaced with fluorine atoms, such as perfluoromethane, clearly fall within this definition. A 1987 DuPont publication entitled "Freon Fluorocarbons Properties and Applications," copy attached, also defines "freons" as "organic compounds containing one or more carbon atoms and fluorine. Chlorine, bromine and hydrogen atoms also may be present."

As of April 1990, one of skill in the art of chemistry would have understood that the phrase "halogenated hydrocarbons" included fluorinated hydrocarbons wherein the "halogen" was fluorine; fluorine is a halogen.

That as of April 1990, one of ordinary skill in the art would be aware that the fluorinated hydrocarbon gases as exemplified by the "freons" include various fluorine-containing members that would themselves be physiologically acceptable to form stable microbubble suspensions suitable for injection into living organisms for the purposes of echographic imaging and the like as evidenced, for instance, by the toxicity data provided in the attached DuPont "Freon" brochures among other documents available to those skilled in this art. Such gases would include gases which are predominantly fluorinated such as CF_4 , CClF_3 , C_2ClF_5 , $\text{C}_2\text{Cl}_2\text{F}_4$, C_3F_8 , C_4F_{10} , etc.

SCHNEIDER et al
Serial No. 08/893,371

I declare further that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

Date: May 7th, 1998

Michel Schneider
Michel Schneider



G-1

"FREON" FLUOROCARBONS Properties and Applications

TABLE OF CONTENTS

I. Table of "Freon" Compounds	2
II. Safety.....	2
A. Flammability	
B. Toxicity	
i. Relative Toxicity and the TLV	
ii. Dermal	
iii. Oral	
iv. CNS Effects	
v. Cardiac Sensitization	
C. Thermal Decomposition	
D. Major Spills and Vapor Releases	
III. Physical and Chemical Properties	4
A. Physical Properties*	
B. Chemical Properties	
i. Thermal Stability	
ii. Reactions with Other Materials	
a. Air	
b. Water (Hydrolysis)	
c. Lubricating Oils (Hydrocarbons)	
d. Metals	
e. Plastics	
f. Elastomers	
C. Solubility Properties	
IV. Applications.....	8
V. Pressure Temperature Relationships.....	10
VI. Miscellaneous	11
VII. References	11

*also see Table VIII, p 9



I TABLE OF "FREON" COMPOUNDS

TABLE I				
Product	Formula	Molecular Weight	Boiling Point	
			°F	°C
"Freon" 14	CF ₄	88.0	-198.3	-128.0
"Freon" 503	CHF ₃ CClF ₃	87.3	-127.6	-88.7
"Freon" 23	CHF ₃	70.0	-115.7	-82.0
"Freon" 13	CClF ₃	104.5	-114.6	-81.4
"Freon" 116	CF ₃ -CF ₃	138.0	-108.8	-78.2
"Freon" 13B1	CBrF ₃	148.9	-72.0	-57.8
"Freon" 502	CHClF ₂ CClF ₂ -CF ₃	111.6	-49.8	-45.4
"Freon" 22	CHClF ₂	86.5	-41.4	-40.8
"Freon" 115	CClF ₂ -CF ₃	154.5	-38.4	-39.1
"Freon" 500	CCl ₂ F ₂ CH ₃ CHF ₂	99.3	-28.3	-33.5
"Freon" 12	CCl ₂ F ₂	120.9	-21.6	-29.8
"Freon" 114	CClF ₂ -CClF ₂	170.9	38.8	3.8
"Freon" 11	CCl ₃ F	137.4	74.9	23.8
"Freon" 113	CCl ₂ F-CClF ₂	187.4	117.6	47.6

The "Freon" products are organic compounds containing one or more carbon atoms and fluorine. Chlorine, bromine and hydrogen atoms also may be present. Their principal characteristics include non-flammability, low toxicity, excellent thermal and chemical stability, high density coupled with low boiling point, low viscosity and low surface tension. A brief discussion of their properties and applications is given on the following pages. Further information on specific subjects is available from the "Freon" Products Division.

II. SAFETY.

Although the "Freon" compounds have relatively low toxicities compared with most chemicals, users should be familiar with Section II.

A. Flammability

None of the "Freon" compounds is flammable or explosive. However, mixtures with flammable liquids or gases may be flammable and should be handled with caution.

B. Toxicity

Potential hazards of fluorocarbons are summarized in Table II. Specific hazards are discussed below.

I. Relative Toxicity and the Threshold Limit Value

A Threshold Limit Value (TLV) has been established by the American Conference of Governmental Industrial Hygienists (ACGIH) for a number of compounds in common use. These values are

"airborne concentrations of substances (representing) conditions under which it is believed that nearly all workers may be repeatedly exposed day after day without adverse effect ... TLV's refer to time-weighted concentrations for a 7- or 8-hour work day and 40-hour work week". Based on both experiment and experience, TLV's provide a quantitative assessment of the relative toxicity of compounds. The TLV is customarily expressed in parts per million by volume, abbreviated ppm.

With the exceptions of "simple asphyxiants" (such as nitrogen) and also carbon dioxide (TLV 5000 ppm, a unique compound since it is a normal product of respiration), the range of TLV's extends from 0.001 ppm (most toxic) to 1000 ppm (least toxic). Where TLV's have been assigned to individual "Freon" fluorocarbons, all are 1000 ppm, except "Freon" 11 which has a ceiling limit of 1,000 ppm. (See Table VIII on page 9).

Exposure to chemicals should be minimized and should not exceed the TLV. Since the TLV is a time-weighted concentration, some provision is made for temporary excursions above the TLV. Details of the TLV, permissible excursions and the TLV for mixtures of compounds are more fully explained in Reference 9.

II. Dermal Effects (Skin Contact)

Including Eye Contact

Liquid fluorocarbons with boiling points below 0°C (32°F) may freeze the skin on contact causing frost-bite. Suitable protective gloves and clothing

TABLE II
Potential Hazards of Fluorocarbons

Condition	Potential Hazard	Safeguard
Vapors may decompose in flames or in contact with hot surfaces.	Inhalation of toxic decomposition products.	Good ventilation. Irritant decomposition products serve as warning agents.
Vapors are 4 to 5 times heavier than air. High concentrations may tend to accumulate in low places.	Inhalation of concentrated vapors can be fatal.	Avoid misuse. Forced-air ventilation at the level of vapor.
Deliberate inhalation to produce intoxication.	Can be fatal.	Use breathing devices with air supply. Use lifelines when entering tanks or other confined areas.
Some fluorocarbon liquids tend to remove natural oils from the skin.	Irritation of skin.	Do not administer epinephrine or other similar drugs.
Lower boiling liquids may be splashed on skin.	Freezing.	Use gloves and protective clothing.
Liquids may be splashed into eyes.	Lower boiling liquids may cause freezing. Higher boiling liquids may cause temporary irritation and if other chemicals are dissolved, may cause serious damage.	Use gloves and protective clothing.
Contact with highly reactive metals.	Violent explosion may occur.	Wear eye protection. Get medical attention. Flush eyes for several minutes with running water.
		Test the proposed system and take appropriate safety precautions.

give insulation protection. Eye protection should be used. In the event of frost-bite, warm the affected area quickly to body temperature. Eyes should be flushed with water copiously. Hands may be held under armpits or immersed in warm water. Get medical attention promptly.

Fluorocarbons with boiling points at or above ambient temperature tend to dissolve protective fat from the skin, leading to skin dryness and irritation, particularly after prolonged or repeated contact. Such contact should be avoided by using rubber or plastic gloves. Eye protection and face shields should be used if splashing is possible. If irritation occurs following accidental contact, seek medical attention.

iii. Oral Toxicity

Fluorocarbons have low oral toxicity as judged by single dose administration or repeated dosing over long periods of time. When "Freon" 11 and 114 were fed to rats and dogs for 90 days, there were no adverse effects relative to nutritional, biochemical, hematological, urine analytical, or histopathological indices, even at the highest dose levels tested. A two-year feeding study on "Freon" 12 resulted in similar findings. In addition, there were no adverse effects of "Freon" 12 on mutagenic, teratogenic, or three-generation reproductive indices.

However, direct contact of liquid fluorocarbons with lung tissue (aspiration) can result in chemical pneumonitis, pulmonary edema, and hemorrhage.

"Freon" 11 (B.P. 23.8 C) and 113 (B.P. 47.6 C), like many petroleum distillates, are fat solvents and can produce such an effect. If products containing these fluorocarbons were accidentally or purposely ingested, induction of vomiting would be contraindicated.

iv. Central Nervous System (CNS) Effects

Inhalation of concentrated vapors of the fluorocarbons can lead to CNS effects comparable with the effects of general anesthesia. Symptoms, as the extent of exposure increases, are initially a feeling of intoxication, followed by loss of coordination and unconsciousness. Under severe conditions, death can result. If these symptoms are felt, the exposed individual should immediately go or be moved to fresh air. Medical attention should be sought promptly. See also II.b.v.—Cardiac Sensitization (below). Individuals exposed to fluorocarbons must not be treated with adrenalin (epinephrine).

v. Cardiac Sensitization

In common with a number of volatile, water-insoluble organic liquids, fluorocarbons can, in sufficient vapor concentration, produce cardiac sensitization. Cardiac sensitization is a sensitization of the heart to adrenaline brought about by exposure to high concentrations of organic vapors. Under conditions of sufficiently severe exposure, cardiac arrhythmias may result from sensitization of the heart to the body's own levels of adrenaline, particularly under conditions of emotional or physical

stress, fright, panic, etc. (Reference 10) Such cardiac arrhythmias may result in ventricular fibrillation and death. As indicated in II.b.iv above, exposed individuals should go or be removed to fresh air promptly (where the hazard of cardiac effects will rapidly decrease). Prompt medical examination and observation should be provided following accidental exposures. A worker adversely affected by fluorocarbon vapors should not be treated with adrenalin (epinephrine) or similar heart stimulants since these would increase the risk of cardiac arrhythmias.

C. Thermal Decomposition Products

Fluorocarbons decompose when exposed directly to high temperatures. Flames and electrical resistance heaters, for example, will cause pyrolysis of fluorocarbon vapors. Products of this decomposition in air include halogens and halogen acids (hydrochloric, hydrofluoric and hydrobromic), as well as other irritating compounds. Although much more toxic than the parent fluorocarbon, these decomposition products tend to irritate the nose, eyes and upper respiratory systems, thereby providing a warning of their presence. The practical hazard is relatively slight since it is difficult for a person to remain voluntarily in the presence of decomposition products at concentrations where physiological damage occurs.

When such irritating decomposition products are detected, the area should be evacuated, ventilated, and the source of the problem corrected.

Such thermal decomposition products can be formed when vapors are drawn through lighted tobacco. Smoking should not be permitted in the presence of fluorocarbon vapors.

D. Major Spills and Vapor Releases

Although the toxicity of fluorocarbons is low, the possibility of serious injury or death exists under unusual or uncontrolled exposures or in deliberate abuse by inhalation of concentrated vapors. Since fluorocarbon vapors are more dense than air, high concentrations may form in low-lying areas and persist under poorly ventilated or still air conditions. Personnel should be immediately evacuated from enclosed areas in the event of a large spill or leak, and not return until the contaminated area has been well ventilated. For "Freon" 12, the Threshold Limit Value (TLV) corresponds to approximately one-third of a pound of "Freon" 12 vapor per 1000 cu. ft. of air (about 5 grams/cubic meter).

Emergency access to areas containing high concentrations of fluorocarbons (e.g., into a vapor-filled storage tank) requires the use of self-contained breathing apparatus and experienced supervision.

III. PHYSICAL AND CHEMICAL PROPERTIES

A. Physical Properties

The unusual combination of physical properties found in the "Freon" compounds is the basis for their application and usefulness. Uses and a summary of physical properties are given in Tables VII and VIII (pages 8 & 9). Typically, the compounds have high molecular weight in relation to the boiling point, low viscosity, low surface tension, and low latent heats of freezing and vaporization. Low conductivity and good dielectric properties are also found. Additional details on thermodynamic properties of individual "Freon" compounds are available on request.

B. Chemical Properties

I. Thermal Stability

The hazards from the thermal decomposition of fluorocarbons are discussed in Section II.C, page 4.

The "Freon" fluorocarbons will not decompose by the application of heat alone except at very high temperatures. Table III lists the temperatures to which various compounds were heated to obtain measurable decomposition rates. Shown also are the temperatures at which decomposition rates are calculated to be 1% per year. The latter can be considered to be the temperature limits imposed by the inherent stability of the molecules.

TABLE III
Fluorocarbon Decomposition Temperatures

Fluorocarbon	Decomposition Temperature*	
	Lab Test**	1%/year†
"Freon" 11	590°C (1100°F)	>300°C (>570°F)
"Freon" 12	760°C (1400°F)	>480°C (>900°F)
"Freon" 13	840°C (1550°F)	>535°C (>1000°F)
"Freon" 22	425°C (800°F)	250°C (480°F)
"Freon" 114	590°C (1100°F)	375°C (710°F)
"Freon" 115	625°C (1160°F)	390°C (740°F)

*For the pure compound (in the absence of air)

**The decomposition rate at this temperature is of the order of 1% minute. Tests were run in platinum tubes and except for "Freon" 11, represent homogeneous decomposition rates (no wall effect).

†These temperatures were computed by extrapolating the high temperature rate data.

II. Reactions with Other Materials

When fluorocarbons are heated to high temperatures in contact with other materials (such as

air, moisture, metallic and plastic construction materials, lubricating oils, etc.), chemical reactions may occur between the fluorocarbon and the other material. These proceed at temperatures lower than the values shown in Table III. Also, the products of reaction are different. The temperatures at which significant reaction occurs and the reaction products will be different for each material; therefore, no simple generalization can be made regarding the stability of "Freon" fluorocarbons in combination with other materials. Some important specific cases are considered below.

a. Air

"Freon" 22 at pressures in excess of 150 psi has been found to be mildly combustible with air or oxygen, and it should not be mixed with air for leak testing. No other evidence for interaction of fluorocarbons with air has been found in the wide variety of uses that fluorocarbons have been put to in past several decades, except for exposure of fluorocarbon-air mixtures to extreme temperatures such as flames (where temperatures are upwards from 1650 C [3000 F]) or electric resistance heaters (where temperatures will be over 700 C [1300 F] if the wire is red hot). The reactions that occur here were discussed in Section II.C.

b. Water (Hydrolysis)

The perhalogenated "Freon" compounds do not hydrolyze in the normal sense to carbonic acid derivatives. Rates of hydrolysis in pure water are too low to be measurable, being less than 0.1 grams/liter of water/year at 25 C (77 F). The presence of oxidizable materials can enhance the apparent hydrolysis.

Hydrogen-containing "Freon" 22 and "Freon" 23 hydrolyze at rates proportional to the concentration in solution and the hydroxylion concentration. Table IV gives the measured hydrolysis rates in sodium hydroxide solution and extrapolated values in pure water.

c. Lubricating Oils (Hydrocarbons)

The stability of "Freon" fluorocarbons with lubricating oils has been amply demonstrated by their successful use for many years in refrigeration systems. In small hermetic systems where "Freon" 12, "Freon" 22, and "Freon" 502* are used, oil-fluorocarbon mixtures are exposed to electric motors operating as high as 107°C (225 F). At the discharge valve of the compressor, mixtures of fluorocarbon gas and oil mist may be at temperatures of 177°C (350 F) and higher, but the exposure time is brief. Table V lists the suggested maximum temperatures for continuous exposure of various "Freon" fluorocarbons in contact with oil and metals.

If the stability limits are exceeded, a chemical reaction occurs between the refrigerant and the oil. For some fluorocarbons, such as "Freon" 12 and 22, the reaction is believed to involve the interchange of a chlorine atom from the fluorocarbon with a hydrogen atom from the oil. The resulting chlorinated oil may break down to hydrochloric acid and unsaturated oil which, in turn, may polymerize to a degraded oil and ultimately a sludge.

*Azeotropic mixture of "Freon" 22 and "Freon" 115

TABLE IV
Hydrolysis Rate in Grams/Liter of Water/Hour
Saturated Conditions at 25 C (77 F)

Compound	in Water Only	in 10% Sodium Hydroxide Solution
"Freon" 22	1.40×10^{-6}	2.2×10^{-1}
"Freon" 23	3×10^{-10}	1.6×10^{-4}

TABLE V
Thermal Stabilities of "Freon" Compounds

Compound	Formula	Maximum Temperature for Continuous Exposure in the Presence of Oil, Steel and Copper, °C (°F)	Decomposition Rate at 204°C (400°F) in Steel, Percent/Year (a)
"Freon" 11	CCl_3F	107 (225)	2
"Freon" 113	$\text{CCl}_2\text{F}-\text{CClF}_2$	107 (225)	6
"Freon" 12	CCl_2F_2	121 (250)	<1
"Freon" 114	$\text{CClF}_2-\text{CClF}_2$	121 (250)	1
"Freon" 22	CHClF_2	149 (300)	(b)
"Freon" 13	CClF_3	>149 (>300)	(b)

(a) no oil present
(b) not measured

d. Metals

Most of the commonly-used construction metals-such as steel, cast iron, brass, copper, tin, lead, aluminum-can be used satisfactorily with the "Freon" compounds under normal conditions of use. At high temperatures, some of the metals may act as catalysts for the breakdown of the compound. The tendency of metals to promote thermal decomposition of the "Freon" compounds is in the following general order:

Least decomposition: Inconel < 18-8 stainless steel < nickel < 1340 steel < aluminum < copper < bronze < brass < silver. Most decomposition. This order is only approximate and exceptions may be found for individual "Freon" compounds or for special conditions of use.

Magnesium alloys and aluminum containing more than 2 percent magnesium are not recommended for use in systems containing "Freon" compounds where water may be present.

Zinc is not recommended for use with "Freon" 11 or "Freon" 113. Experience with zinc and the other "Freon" compounds has been limited and no unusual reactivity has been observed. However, it is somewhat more chemically reactive than other common construction metals, and it would seem wise to avoid its use with the "Freon" compounds unless adequate testing is carried out.

Metals which may be questionable for use in applications requiring contact with the "Freon" compounds for long periods of time or unusual conditions of exposure, however, can be cleaned safely with "Freon" solvents. Cleaning applications are usually for short exposures at moderate temperatures.

Halocarbons may react violently with highly reactive materials such as the alkali and alkaline earth metals, sodium, potassium, and barium, etc., in their free metallic form. Materials become more reactive when finely ground or powdered, and in this state magnesium and aluminum may react with fluorocarbons, especially at higher temperatures. Highly reactive materials should not be brought into contact with fluorocarbons until a careful study is made and appropriate safety precautions are taken.

e. Compatibility with Plastics

A brief summary is given below. Differences in polymer structure, molecular weight, plasticizer type and content and temperature may result in significant changes in the resistance of plastics to "Freon" compounds. Thus, compatibility tests should be made for specific applications.

ABS Plastics-Considerable variation in resistance with specific formulations is found. Careful testing is required.

Acetal Resins-Suitable for use with "Freon" compounds under most conditions.

Acrylic Fiber (polyacrylonitrile)-Generally suitable for use with "Freon" compounds.

Acrylic Resin (methacrylate polymers) - May be dissolved by "Freon" 22, but is generally suitable for use with "Freon" 12 and "Freon" 114, particularly for short exposures. On long exposure, cracking and crazing may occur, and the plastic may become cloudy. Use with "Freon" 113 and "Freon" 11 is questionable and should be carefully tested.

Cast resins are usually significantly more resistant than extruded resin.

Cellulose Acetate and Cellulose Nitrate-Generally suitable for use with "Freon" compounds.

Epoxy Resins-Highly resistant when cured and normally completely suitable for use with "Freon" compounds.

Nylon-Generally suitable but may tend to embrittle at high temperatures in the presence of air or water. Tests at 121°C (250°F) with "Freon" 12 and "Freon" 22 indicated the presence of water or alcohol to be undesirable. Testing required, particularly for high temperature service.

Phenolic Resins-Usually unaffected by "Freon" compounds. Resins of this type encompass a wide range of compositions, and testing is recommended.

Polycarbonate Resin-usually undergoes considerable swelling and extraction. Not recommended.

Polychlorotrifluoroethylene-Slight swelling, but generally suitable for use with the "Freon" compounds.

Polyethylene and Polypropylene-Usually suitable for room temperature applications. Resistance to "Freon" compounds becomes more variable as temperatures are increased.

Polystyrene-Considerable variation in resistance is found. Some applications with "Freon" 114 may be satisfactory. Generally use with "Freon" compounds is not satisfactory. Careful testing is required. Generally less suitable for use with fluorocarbons than ABS plastics.

Polyvinyl Alcohol-Not affected by "Freon" compounds, but highly sensitive to water. Used in tubing for fluorocarbon service with an outer protective covering.

Polyvinyl Chloride and Other Plastics—Resistance to "Freon" compounds depends on the vinyl type and the amount and type of plasticizer. Testing required.

Silicone Resin—Generally extensively swollen. Not recommended.

TFE-Fluorocarbon Resin—No swelling observed in "Freon" liquids, but diffusion through the resin occurs with "Freon" 12 and "Freon" 22.

I. Compatibility with Elastomers

Considerable variation is found in the effect of the "Freon" compounds on elastomers depending on the particular compound and elastomer type. In nearly all cases, a satisfactory combination can be found. In some instances, the presence of other materials such as oils may give unexpected results, so preliminary testing of the system is recommended.

Comparison of the linear swelling of elastomers often provides an indication of their suitability for use with the "Freon" compounds. Such a comparison is given in Table VI.

Swelling tests conducted by immersing the elastomers in the liquid until equilibrium or maximum swelling was reached. Elastomers which swell excessively are not recommended for applications requiring long exposure. In many cases, however, parts containing such elastomers can be cleaned safely with "Freon" solvents when the exposure is relatively short.

Additional data are available in our Bulletin B-12A.

C. Solubility Properties

The solvent power of the "Freon" compounds varies from poor for "Freon" 115, "Freon" 114 and "Freon" 12 to fairly good for "Freon" 11, "Freon" 22, and "Freon" 113. Typical non-polar liquids, the fluorocarbons are good solvents for other non-polar materials and poor solvents for polar compounds. The solubilities of water in "Freon" compounds and of "Freon" compounds in water are low. Lubricating oils are generally miscible with "Freon" compounds at room temperature, although separation may occur at low temperatures. Water solubility is shown in Table VIII.

TABLE VI
Swelling of Elastomers by "Freon" Fluorocarbons and Other Compounds

Product	Percent Increase in Length at Room Temperature					
	Neoprene GN	Buna N (butadiene/acrylonitrile)	Buna S (butadiene/styrene)	Butyl (isoprene/isobutylene)	Polysulfide Type	Natural Rubber
"Freon" 11	17	6	21	41	2	23
"Freon" 12	0	2	3	6	1	6
"Freon" 13	0	1	1	0	0	1
"Freon" 22	2	26	4	1	4	6
"Freon" 113	3	1	9	21	1	17
"Freon" 114	0	0	2	2	0	2
"Freon" 115	0	0	0	0	0.2	0
"Freon" 502	1	7	3	1.6	1.6	4
"Freon" 1381	2	1	1	2	0	1
Methyl chloride	22	35	20	16	11	26
Methylene chloride	37	52	26	23	59	34
Methyl chloroform (1,1,1-trichloroethane)	54	24	44	35	12	59

IV APPLICATIONS OF "FREON" FLUOROCARBON COMPOUNDS

TABLE VII

The table below is intended to provide a general view of the range of applications and is not all-inclusive. For specialized applications or more detail, please make specific request.

Fluorocarbon	Refrigerants	Aerosol Propellants	Solvents, Blowing Agents, Fire Extinguishants, Dielectric Fluids and Other Uses
"Freon" 14	Specialty low temperature applications.	—	Plasma etchant.
"Freon" 23	Component of "Freon" 503 azeotrope	—	Plasma etchant.
"Freon" 13	Specialty low temperature applications.	—	Plasma etchant.
"Freon" 116	Specialty low temperature applications.	—	Dielectric gas, Plasma etchant
"Freon" 13B1	Intermediate between "Freon" 13 and "Freon" 22 for medium to low temperature applications. Not extensively used.	—	Efficient fire extinguishant (Halon® 1301) especially suited for automatic protection of materials subject to water damage and of areas occupied by personnel.
"Freon" 22	Household and commercial refrigeration and air conditioning applications. Permits use of smaller equipment. Component of azeotropes	High pressure propellant for non-food uses	—
"Freon" 115	Used as an azeotrope component in "Freon" 502	Accepted as a food propellant by the FDA, this material is well suited for food aerosols and finds use in fat emulsion food whips. Good foam stability with absence of odor or taste	Dielectric fluid, an economic replacement for "Freon" 116 in most dielectric applications. Plasma etchant.
"Freon" 12	Most widely used refrigerant in household, automotive and commercial refrigeration and air conditioning systems. Also as a component of azeotropes and, in high purity form ("Freon" freazant) approved as a direct contact freezing agent for foods.	High pressure propellant for EPA exempted products.	Blowing agent for foamed plastics applications. Dielectric gas.
"Freon" 114	In large industrial process cooling and air conditioning systems using multi-stage centrifugal compressors.	Low pressure propellant, alternative to "Freon" 11, having poorer solubility properties and less odor. Especially used in personal products.	Blowing agent for foamed plastics
"Freon" 11	Widely used in centrifugal compressors for industrial and commercial air conditioning systems and for industrial cooling of process water or brine. Low viscosity and freezing point permit use as a low-temperature cooling liquid.	Low pressure propellant for EPA exempted products.	Occasionally used as a solvent ("Freon" MF). Blowing agent for foamed plastics.
"Freon" 113	In commercial and industrial air conditioning and process water or brine chilling using centrifugal compressors, particularly in small tonnage applications.	Solvent in some aerosol formulations, usually propelled with "Freon" 12	Extensively as a solvent ("Freon" TF) alone and in special purpose formulations for a wide range of critical cleaning needs. In cutting fluid formulations, reaction media, extractant, etc.

TABLE PHYSICAL PROPERTIES

	"FREON" 11	"FREON" 12	"FREON" 13	"FREON" 13B1	"FREON" 14	"FREON" 22
Chemical Formula	CCl_2F	CCl_2F_2	CClF_3	CBrF_3	CF_4	CHClF_2
Molecular Weight	137.37	120.92	164.46	146.92	88.00	86.47
Boiling Point at 1 atm	°C 74.87	-23.79 -21.62	-81.4 -114.6	-57.75 -71.95	-127.96 -198.32	-40.75 -61.36
Freezing Point	°C -168	-158 -252	-181 -294	-168 -270	-184 -299	-160 -256
Critical Temperature	°C 198.0	112.0	28.9	67.0	-45.67	96.0
Critical Pressure	atm 50.5	23.6	83.9	152.6	-50.2	204.8
Critical Volume	cc/mol 0.0289	0.0287	0.0277	0.0215	0.0256	0.0205
Critical Density	g/cc 34.6	0.558	0.578	0.745	0.626	0.525
Density, Liquid at 25°C (77°F)	g/cc 1.478	1.311	1.298	1.538	1.317	1.194
Density, Saturated Vapor at Boiling Point	g/l 0.367	0.33	0.438	0.71	0.476	0.295
Specific Heat, Liquid (Heat Capacity) at 25°C (77°F)	cal (g) (°C) 0.208	0.232	0.247	0.208	0.294	0.300
Specific Heat Vapor, at Const Pressure (1 atm) at 25°C (77°F)	cal (g) (°C) 0.142	0.145	0.158	0.112	0.163	0.157
Specific Heat Ratio at 25°C and 1 atm	C_p/C_v 1.137	1.137	1.145	1.144	1.159	1.184
Heat of Vaporization at Boiling Point	cal/g 43.10	39.47	35.47	28.38	32.49	55.81
Thermal Conductivity* at 25°C (77°F)						
Liquid	0.0506	0.0405	0.0378	0.0234	0.0361	0.0507
Vapor (1 atm)	0.00451	0.00557	0.00501	0.00534	0.00463	0.00609
Viscosity* at 25°C (77°F)						
Liquid	0.415	0.214	0.170	0.157	0.23	0.198
Vapor (1 atm)	0.0107	0.0123	0.0119	0.0154	0.0116	0.0127
Surface Tension at 25°C (77°F)	dynes/cm 18	9	14	4	4	8
Refractive Index of Liquid at 25°C (77°F)	1.374	1.287	1.199	1.238	1.151	1.256
Relative Dielectric Strength* at 1 atm and 25°C (77°F) (nitrogen = 1)	3.71	2.46	1.65	1.83	1.06	1.27
Dielectric Constant Liquid Vapor (1 atm)	2.78 1.0036	2.13 1.0032	1.0024	1.0012	1.0012	6.11
Solubility of "Freon" in Water at 1 atm and 25°C (77°F)	wt % 0.11	0.028	0.009	0.03	0.0015	0.30
Solubility of Water in "Freon" at 25°C (77°F)	wt % 0.011	0.009		0.0095		0.13
Toxicity* Threshold Limit Value (TLV)	ppm (v/v) 1000	1000	Less toxic than "Freon" 12	1000	Less toxic than "Freon" 12	1000

*FREON is Du Pont's registered trademark for its fluorocarbon products.
* ceiling limit

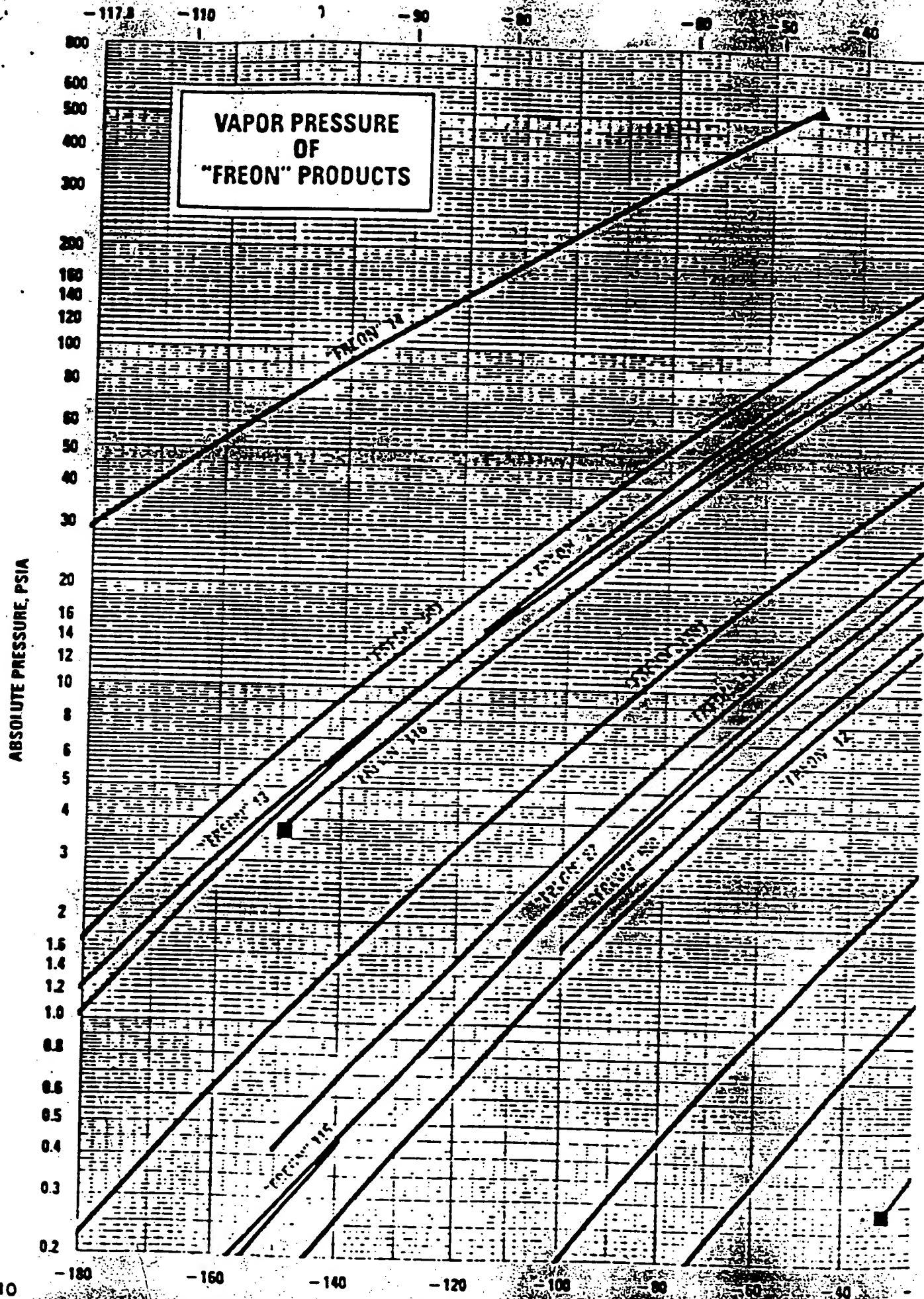
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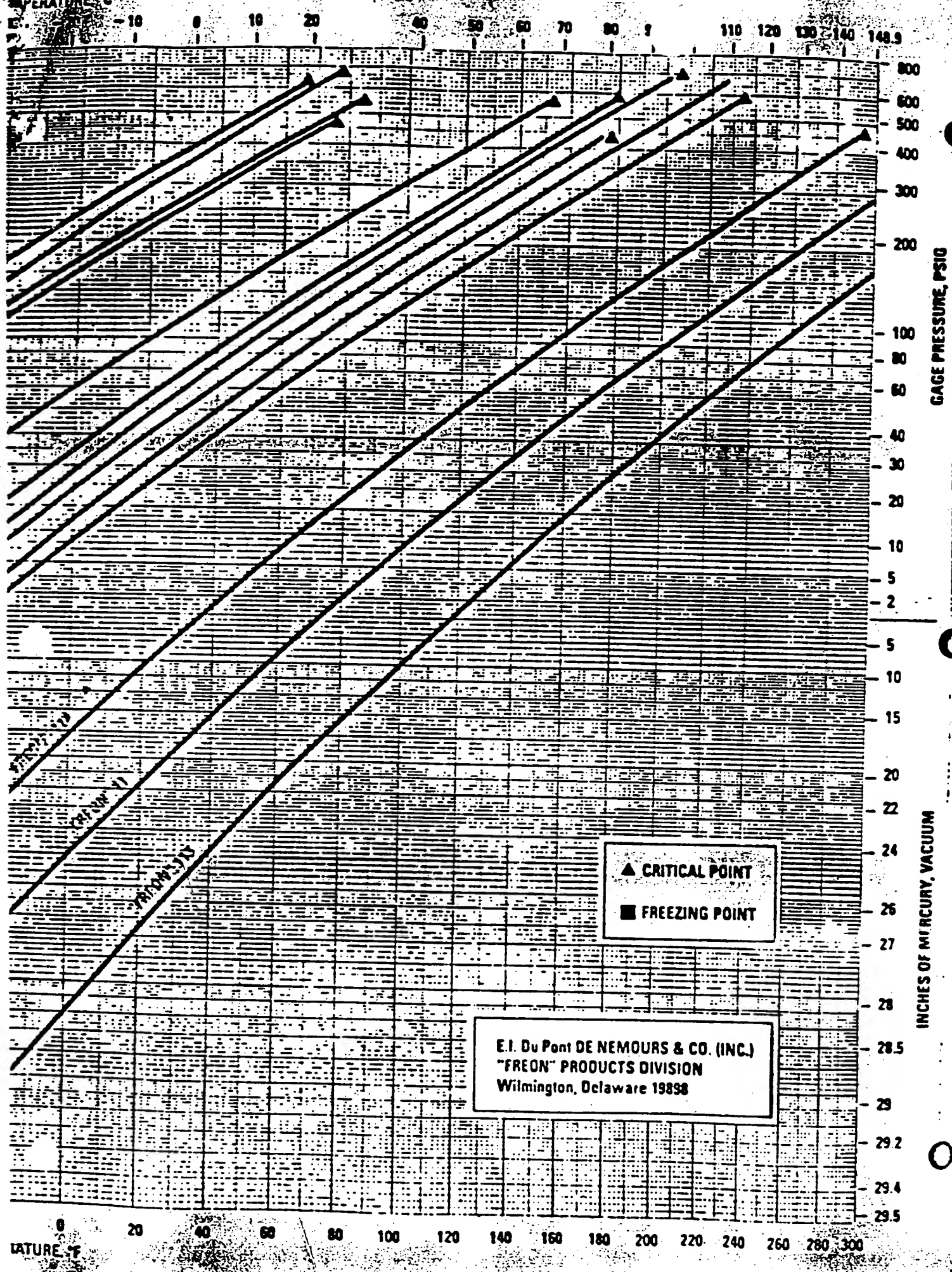
ES OF FREON* PRODUCTS

FREON 22	FREON 113	FREON 114	FREON 115	FREON 116	FREON 120	FREON 122	FREON 123
CH ₂ F ₂	CCl ₃ F-CCl ₂ F	CCl ₂ F ₂ -CCl ₂ F ₂	CCl ₂ F ₂ -CF ₃	CF ₃ -CF ₃	0	0	C
78.01	187.38	178.93	154.47	138.01	98.31	111.84	87.28
-82.83 -118.85	47.57 117.53	2.77 38.78	-39.1 -38.4	-78.2 -108.8	-23.5 -28.3	-48.42 -48.76	-88.7 -127.6
-198.2 -267.6	-25 -31	-94 -137	-108 -158	-180.6 -148.1	-158 -254		
25.9 78.8	214.1 417.4	145.7 284.3	80.0 175.9	19.7 67.5	185.5 221.9	82.2 179.9	19.5 67.1
47.7 781.4	33.7 495	32.2 473.2	30.8 453	29.4 432	43.67 641.9	48.2 581.0	43.0 632.7
133 8.0305	325 8.0278	293 8.0275	259 8.0269	225 8.0262	200.0 8.0226	188 8.0257	155 8.0284
0.525 32.78	0.576 38.0	0.582 38.32	0.596 37.2	0.612 38.21	0.4984 31.8	0.561 35.0	0.564 35.21
8.670 41.82	1.565 97.69	1.456 90.91	1.291 80.60	1.587 ^b 99.08	1.156 72.18	1.217 75.95	1.233 ^c 76.95
0.66 0.291	7.38 0.461	7.83 0.489	8.37 0.522	9.01 ^b 0.562	5.278 0.3295	6.22 0.388	6.02 0.374
0.345 ^a -30°C (-22°F)	0.218	0.243	0.285	0.232 ^a -73°C (-100°F)	0.258	0.293	0.287 ^a -30°C (-22°F)
0.176	0.181 ^a 80°C (140°F)	0.170	0.164	0.182 ^a at 0 pressure	0.175	0.164	0.16
1.191 ^a at 0 pressure	1.080 ^a 80°C (140°F)	1.084	1.091	1.085 ^a rest at 0 pressure	1.143	1.132	1.21 ^a -34°C (-29°F)
57.23 103.62	35.07 63.12	32.51 58.53	30.11 54.20	27.97 50.35	48.04 86.47	41.21 74.18	42.86 77.15
0.0563 ^a -30°C 0.0860 ^a (-22°F)	0.0434 0.0544 10.5 atm	0.0372 0.0060	0.0302 0.00724	0.045 ^a -73°C 0.0098 ^a (-100°F)	0.0432	0.0373 0.00670	0.0430 ^a -30°C (-22°F)
0.167 ^a 30°C 0.0118 ^a (-22°F)	0.68 0.010 10.1 atm	0.36 0.0112	0.183 0.0125	0.30 0.0148	0.182 0.0120	0.180 0.0126	0.144 ^a -30°C (-22°F)
15.16 ^a -73°C (-100°F)	17.3	12	5	16 ^a -73°C (-100°F)	8.4	5.9	6.1 ^a -30°C (-22°F)
1.215 ^a -73°C (-100°F)	1.254	1.288	1.214	1.206 ^a -73°C (-100°F)	1.273	1.234	1.209 ^a -30°C (-22°F)
1.84	3.9 (0.44 atm)	3.34	2.54	2.82		1.3	
1.8873 ^a 25°C ^b	2.41 ^a 25°C (77°F)	2.26 ^a 25°C 1.0043 ^a 26.8°C	1.0035 ^a 27.4°C	1.0021 ^a 23°C (73°F)		6.11 ^a 25°C 1.8036 ^a 10.5 atm	
0.10	0.017 (Sat'n Pres)	0.013	0.005				0.042
	0.011	0.009			0.056	0.056	
is toxic than Freon 22	1000 7600	1000 7600	Less toxic than Freon 114	Less toxic than Freon 114			

**See page 11 for references to data sources.

a CCl₃F, CH₂Cl₂, (75.9°F, 10.5 atm)
b CHCl₃, CCl₄, CF₄, (48.8°F, 10.5 atm)
c CH₂Cl₂, (40.6°F, 10.5 atm)





E. I. Du Pont DE NEMOURS & CO. (INC.)
"FREON" PRODUCTS DIVISION
Wilmington, Delaware 19898



FREON

B-2

Better Things for Better Living
through Chemistry

PROPERTIES AND APPLICATIONS OF THE

"FREON" FLUOROCARBONS

The "Freon" products are organic compounds containing one to four carbon atoms and fluorine. Chlorine, bromine and hydrogen atoms also may be present. Their principal characteristics include nonflammability, a low level of toxicity, excellent thermal and chemical

stability, high density coupled with low boiling point and low viscosity and surface tension. A brief discussion of their properties and applications is given on the following pages. Further information on specific subjects is available from the "Freon" Products Division.

"FREON" COMPOUNDS

Product	Formula	Molecular Weight	Boiling Point	
			°F	°C
"FREON-14"	CF ₄	88.0	-198.4	-128.0
"FREON-23"	CHF ₃	70.0	-115.7	-82.0
"FREON-13"	CClF ₃	104.5	-114.6	-81.4
"FREON-116"	CF ₃ -CF ₃	138.0	-108.8	-78.2
"FREON-13B1"	CBrF ₃	148.9	-72.0	-57.8
"FREON-502"	CHClF ₂ /CClF ₂ -CF ₃ (48.8/51.2% by weight)	111.6	-50.1	-45.6
"FREON-22"	CHClF ₂	86.5	-41.4	-40.8
"FREON-115"	CClF ₂ -CF ₃	154.5	-37.7	-38.7
"FREON-12"	CCl ₂ F ₂	120.9	-21.6	-29.8
"FREON-C318"	C ₃ F ₈ (cyclic)	200.0	21.5	-5.8
"FREON-114"	CClF ₂ -CClF ₂	170.9	38.8	3.8
"FREON-21"	CHCl ₂ F	102.9	48.1	8.9
"FREON-11"	CCl ₃ F	137.4	74.8	23.8
"FREON-114B2"	CBrF ₂ -CBrF ₂	259.9	117.1	47.3
"FREON-113"	CCl ₂ F-CClF ₂	187.4	117.6	47.6
"FREON-112"	CCl ₂ F-CCl ₂ F	203.9	199.0	92.8

OTHER FLUORINATED COMPOUNDS

Product	Formula	Molecular Weight	Boiling Point	
			°F	°C
1,1-Difluoroethane	CH ₃ -CHF ₂	66.1	-12.5	-24.7
1,1,1-Chlorodifluoroethane	CH ₃ -CClF ₂	100.5	14.4	-9.8
1-Fluoro-2,2-dichloroethane	CH ₂ -CHF	46.0	-97.5	-72.0
1,1-Difluoroethylene	CH ₂ =CF ₂	64.0	-122.3	-85.7

PROPERTIES

STABILITY—The "Freon" compounds in general are stable to a degree not ordinarily found in organic compounds. Although related, each member of the "Freon" series has a different chemical structure and a different degree of stability. The presence of fluorine atoms in the molecule is responsible for the stability of the compounds and, as a general rule, the more fluorine present the greater the stability.

The stability of an organic compound is directly related to the conditions under which it is used. Considerable variation may be found, depending on the nature of the metals, elastomers, plastics, oils and other materials which may be present.

Since the presence of other materials and the time and general nature of exposure have a definite effect, it is not possible to define the stability of the "Freon" compounds in a precise way which will include all possible applications. As general examples, some thermal stability data are shown in Table I.

In the third column are listed the approximate maximum temperatures recommended for continuous exposure in the presence of oil, steel and copper. This condition would be representative of refrigeration equipment designed to operate for many years. The recommended temperatures are based on laboratory testing but field experience has been in substantial agreement.

Some actual observed decomposition rates at 400° F in steel are shown in the fourth column. They are based on exposures of six days and disregard a higher rate indicated on initial exposure.

In the last column, decomposition temperatures are illustrated for moderate conditions. No metals were present in these tests and the exposure time was 30 seconds. "Freon-13" was not included in the tests but other evidence indicates that it is substantially more stable than "Freon-12". The presence of hydrogen in the "Freon-22" molecule in place of one of the chlorine atoms in "Freon-12" apparently promotes the stability of the molecule until a temperature sufficient for the removal of hydrochloric acid (HCl) is reached.

The thermal stability of the "Freon" compounds will probably be between the extremes illustrated in Table I for a particular application.

HYDROLYSIS—The hydrolysis rate for the "Freon" compounds as a group is low compared with other halogenated compounds. Within the group, however, there is considerable variation. Conditions of temperature and pressure and the presence of other materials also greatly affect the rate. Typical hydrolysis rates for the "Freon" compounds and other halogenated compounds are illustrated in Table II.

With water alone at atmospheric pressure, the rate is too low to be determined by the analytical method used. When catalyzed by the presence of steel, the hydrolysis rates are detectable but still quite low. At saturation pressures and a higher temperature, the rates are further increased.

Under neutral or acidic conditions, the presence of hydrogen in the molecule has little effect on the hydrolytic stability. However, under alkaline conditions compounds containing hydrogen, such as "Freon-22" and "Freon-21", tend to be hydrolyzed more rapidly. For additional information on hydrolysis write to our nearest sales office.

Table II. HYDROLYSIS RATE IN WATER
Grams (Liter of Water) (Year)

Compound	1 atm. Pressure 86° F		Saturation Pressure 122° F
	Water Alone	With Steel	With Steel
CH ₃ Cl	•	•	110
CH ₂ Cl ₂	•	•	55
"Freon-113"	<0.005	ca. 50**	40
"Freon-11"	<0.005	ca. 10**	28
"Freon-12"	<0.005	0.8	10
"Freon-21"	<0.01	5.2	9
"Freon-114"	<0.005	1.4	3
"Freon-22"	<0.01	0.1	•

*Not measured

**Observed rates vary

LOW TOXICITY — One of the most important qualities of the "Freon" fluorocarbon compounds is the safety with which they can be handled and used.

Comparisons of the relative toxicity and explosion hazards of the "Freon" compounds with other com-

Table I. THERMAL STABILITY OF "FREON" COMPOUNDS

Compound	Formula	Maximum Temperature for Continuous Exposure in the Presence of Oil, Steel and Copper, ° F	Decomposition Rate at 400° F in Steel, Per Cent/Year	Temperature for First Trace of Decomposition in Quartz, ° F
"Freon-11"	CCl ₃ F	225	2	840
"Freon-113"	CCl ₂ F-CClF ₂	225	6	570
"Freon-12"	CCl ₂ F ₂	250	<1	1000
"Freon-114"	CClF ₂ -CClF ₂	250	1	•
"Freon-22"	CHClF ₂	275-300	•	550
"Freon-13"	CClF ₃	> 300	•	•

*Not measured

monly used materials were made by the Underwriters' Laboratories at their principal office and testing station, 207 East Ohio St., Chicago, Illinois. A summary of the comparative life hazard of these compounds is given in Table III. Gaseous compounds have been divided into six groups according to their toxicity. Group 6 contains compounds with a very low degree of toxicity. "Freon-12" and "Freon-114" are in this category. Group 1, at the other end of the scale, includes very toxic materials such as sulfur dioxide.

The "Freon" compounds are listed by the Underwriters' Laboratories under the general reference: Guide No. 360 EO, Refrigerant. The cards for all products include the reference numbers: MH6494, MH2256, MH3134, MH3072 and MH6493. Individual products are designated by letters as follows:

"Freon-11" = A	"Freon-114" = E
"Freon-12" = B	"Freon-115" = F
"Freon-22" = C	"Freon-502" = H
"Freon-113" = D	

For further information on toxicity write for our Bulletin S-16 or copies of the Underwriters' Laboratories' Reports.

NONFLAMMABILITY—None of the "Freon" compounds are flammable or explosive. Mixtures with air have been tested at temperatures up to 212°F.

MATERIALS OF CONSTRUCTION—Metals. Most of the commonly used construction metals—such as steel, cast iron, brass, copper, tin, lead, aluminum—can be used satisfactorily with the "Freon" compounds under normal conditions of use. At high temperatures some of the metals may act as catalysts for the breakdown of the compound. The tendency of metals to promote thermal decomposition of the "Freon" compounds is in the following general order:

Least decomposition: Inconel < 18-8 stainless steel < nickel < copper < 1340 steel < aluminum < bronze < brass < silver: Most decomposition.

This order is only approximate and exceptions may be found for individual "Freon" compounds or for special conditions of use.

Magnesium alloys and aluminum containing more than 2 per cent magnesium are not recommended for use in systems containing "Freon" where water may be present.

Zinc is not recommended for use with "Freon-113". Experience with zinc and the other "Freon" compounds has been limited and no unusual reactivity has been observed. However, it is somewhat more chemically reactive than other common construction metals and it would seem wise to avoid its use with the "Freon" compounds unless adequate testing is carried out.

Metals which may be questionable for use in applications requiring contact with the "Freon" compounds for long periods of time or unusual conditions of exposure, however, can be cleaned safely with "Freon" solvents. Cleaning applications are usually for short exposures at moderate temperatures.

Table III. UNDERWRITERS' LABORATORIES' CLASSIFICATION OF COMPARATIVE LIFE HAZARD OF GASES AND VAPORS

Group	Definition	Examples
1	Gases or vapors which in concentrations of the order of ½ to 1 per cent for durations of exposure of the order of 5 minutes are lethal or produce serious injury.	Sulfur dioxide
2	Gases or vapors which in concentrations of the order of ½ to 1 per cent for durations of exposure of the order of ½ hour are lethal or produce serious injury.	Ammonia, Methyl bromide
3	Gases or vapors which in concentrations of the order of 2 to 2½ per cent for durations of exposure of the order of 1 hour are lethal or produce serious injury.	Bromochloromethane, Carbon tetrachloride, Chloroform, Methyl formate
4	Gases or vapors which in concentrations of the order of 2 to 2½ per cent for durations of exposure of the order of 2 hours are lethal or produce serious injury.	Dichloroethylene, Methyl chloride, Ethyl bromide
Between 4 & 5	Appear to classify as somewhat less toxic than Group 4.	Methylene chloride, Ethyl chloride "Freon-112"
	Much less toxic than Group 4 but somewhat more toxic than Group 5.	"Freon-113" "Freon-21"
5a	Gases or vapors much less toxic than Group 4 but more toxic than Group 6.	"Freon-11" "Freon-22" "Freon-114B2" "Freon-502" Carbon dioxide
5b	Gases or vapors which available data indicate would classify as either Group 5a or Group 6.	Ethane, Propane Butane
6	Gases or vapors which in concentrations up to at least about 20 per cent by volume for durations of exposure of the order of 2 hours do not appear to produce injury.	"Freon-13B1" "Freon-12" "Freon-114" "Freon-115" "Freon-13" "Freon-14" "Freon-23" "Freon-116" "Freon-C318"

*Not tested by U. L. but estimated to belong in group indicated.

Plastics. A brief summary of the effect of the "Freon" compounds on various plastic materials is given below but compatibility should be tested for specific applications. Differences in polymer structure and molecular weight, plasticizers, temperature, etc., may alter the resistance of the plastic toward the "Freon" compound.

"Teflon" tetrafluoroethylene resin. No swelling observed when submerged in "Freon" liquids but some diffusion found with "Freon-12" and "Freon-22".

Polychlorotrifluoroethylene. Slight swelling but generally suitable for use with the "Freon" compounds.

Polyvinyl alcohol. Not affected by the "Freon" compounds but very sensitive to water. Used especially in tubing with an outer protective covering.

Vinyl. Resistance to the "Freon" compounds depends on vinyl type and plasticizer and considerable variation is found. Samples should be tested before use.

"Orlon" acrylic fiber. Generally suitable for use with the "Freon" compounds.

Nylon. Generally suitable for use with the "Freon" compounds but may tend to become brittle at high temperatures in the presence of air or water. Tests at 250° F with "Freon-12" and "Freon-22" showed the presence of water or alcohol to be undesirable. Adequate testing should be carried out.

Polyethylene. May be suitable for some applications at room temperatures but should be thoroughly tested since greatly different results have been found with different samples.

"Lucite" acrylic resin (methacrylate polymers). Dissolved by "Freon-22" but generally suitable for use with "Freon-12" and "Freon-114" for short exposure. On long exposure tends to crack and craze and become cloudy. Use with "Freon-113" may be questionable and probably should not be used with "Freon-11".

Cast "Lucite" acrylic resin is much more resistant to the effect of solvents than extruded resin and can probably be used with most of the "Freon" compounds.

Polystyrene. Considerable variation found in individual samples but generally not suited for use with the

"Freon" compounds. Some applications might be all right with "Freon-114".

Phenolic resins. Usually not affected by the "Freon" compounds. However, composition of resins of this type may be quite different and samples should be tested before use.

Epoxy resins. Resistant to most solvents and entirely suitable for use with the "Freon" compounds.

Cellulose acetate or nitrate. Suitable for use with the "Freon" compounds.

"Delrin" acetal resin. Suitable for use with the "Freon" compounds under most conditions.

Elastomers. Considerable variation is found in the effect of the "Freon" compounds on elastomers depending on the particular compound and elastomer type. In nearly all cases a satisfactory combination can be found. In some instances the presence of other materials such as oils may give unexpected results so preliminary testing of the system involved is recommended.

Comparison of the linear swelling of elastomers often provides an indication of their suitability for use with the "Freon" compounds. Such a comparison is given in Table IV.

The swelling tests were conducted by immersing the elastomers in the liquid until equilibrium or maximum swelling was reached. Elastomers which swell excessively are not recommended for applications requiring long exposure. In many cases, however, parts containing such elastomers can be cleaned safely with "Freon" solvents when the exposure is relatively short.

Some additional data are available in our Bulletin B-12A.

Table IV. SWELLING OF ELASTOMERS BY "FREON" AND OTHER COMPOUNDS

Product	Per Cent Increase in Length at Room Temperature					
	Neoprene GN	Buna N (butadiene/ acrylonitrile)	Buna S (butadiene/ styrene)	Butyl (isoprene/ isobutylene)	Polysulfide Type	Natural Rubber
"Freon-11"	17	6	21	41	2	23
"Freon-12"	0	2	3	6	1	6
"Freon-13"	0	1	1	0	0	1
"Freon-21"	28	48	49	24	28	34
"Freon-22"	2	26	4	1	4	6
"Freon-113"	3	1	9	21	1	17
"Freon-114"	0	0	2	2	0	2
"Freon-115"	0	0	0	0	0.2	0
"Freon-502"	1	7	3	1.6	1.6	4
"Freon-13B1"	2	1	1	2	0	1
"Freon-114B2"	7	7	15	22	1	26
"Freon-C318"	0	0	0	0	0	0
Methyl chloride	22	35	20	16	11	26
Methylene chloride	37	52	26	23	59	34

SOLUBILITY BEHAVIOR—The solvent power of the "Freon" products ranges from poor for the highly fluorinated compounds such as "Freon-12" and "Freon-114" to fairly good for those containing less fluorine such as "Freon-11" and "Freon-113". They are typical nonpolar liquids and as such are found to be good solvents for other nonpolar materials and poor solvents for highly polar compounds. Some solubility relationships are shown in Table V. The solubility of water is low. Refrigeration lubricating oils are in general miscible at all temperatures, although with "Freon-22", "Freon-114" and "Freon-502" two liquid phases are formed at low temperatures. The Kauri-butanol test is often used to compare the solvent power of industrial solvents. A high number indicates a good solvent.

For further information on solubility behavior write for Bulletins B-7 and FS-1.

Table V. SOLUBILITY RELATIONSHIPS

Product	Solubility of Water at 32° F (0° C), % by Wt.	Oil Solutions	Kauri-butanol Number
"Freon-11"	0.0036	Miscible	60
"Freon-12"	0.0026	Miscible	18
"Freon-21"	0.055	Miscible	102
"Freon-22"	0.060	•	25
"Freon-113"	0.0036	Miscible	32
"Freon-114"	0.0026	•	12
"Freon-502"	0.022	•	14 (est.)

•Two liquid phases at low temperatures.

PHYSICAL PROPERTIES—The unusual combination of properties found in the "Freon" compounds is the basis for their wide application and usefulness. A summary of physical properties is given in the chart on page 9. In many cases additional information on specific properties is available on request.

The presence of fluorine in the molecule in many cases has an effect on the boiling point similar to that of hydrogen but at the same time providing a high molecular weight and nonflammability. For example, methane (CH_4) with a molecular weight of 16 has a boiling point of -258.5°F (-161.4°C). On the other hand, "Freon-14" (CF_4) has a molecular weight of 88 and a boiling point of -198.4°F (-128°C) and is nonflammable. The effect is even more pronounced when chlorine is also present. Methylene chloride (CH_2Cl_2 , molecular weight 85) boils at 105.2°F (40.7°C) while "Freon-12" (CCl_2F_2 , molecular weight 121) boils at -21.6°F (-29.8°C). As a result, the "Freon" compounds are high density materials with low boiling points, low viscosity and low surface tension. As illustrated on page 1, the list of "Freon" products includes compounds with boiling points covering a wide temperature range.

The high molecular weight of the "Freon" compounds also contributes to low vapor specific heat values and fairly low latent heats of vaporization. Tables of thermodynamic properties including enthalpy, entropy, pressure, density and volume for the liquid and vapor are available for the commercial products and for some of those still in the development stage. The data are also presented in chart form with pressure plotted against enthalpy.

"Freon" compounds do not conduct electricity and in general have good dielectric properties.

Table VI. PROPERTIES OF VINYL FLUORIDE, VINYLIDENE FLUORIDE, DIFLUOROETHANE AND CHLORODIFLUOROETHANE

	VF	VF ₂	DFF	CDFF
Chemical Formula	$\text{CH}_2=\text{CHF}$	$\text{CH}_2=\text{CF}_2$	CH_3CHF_2	CH_3CClF_2
Molecular Weight	46.046	64.038	66.054	100.503
Boiling Point, °F	-97.5	-122.3	-12.5	14.4
°C	-72.0	-85.7	-24.7	- 9.8
Freezing Point, °F	-256	—	-179	-203
°C	-160	—	-117	-131
Critical Temperature, °F	130.5	86.2	236.5	278.8
°C	54.7	30.1	113.5	137.1
Critical Pressure, Psia	760	643	652	598
Atm	51.71	43.75	44.37	40.69
Critical Density, grams/cc	0.320	0.417	0.365	0.435
lb/cu ft	19.98	26.03	22.79	27.16
Liquid Density at 77 °F (25° C),				
grams/cc	0.620	0.585	0.895	1.109
lbs/cu ft	38.71	36.52	55.87	69.23
Liquid Viscosity at 77°F (25°C), Centipoises	0.13	—	0.237	0.317

APPLICATIONS

REFRIGERANTS—The "Freon" refrigerants have been one of the major factors responsible for the tremendous growth of the home refrigeration and air-conditioning industries. The safe properties of these products have permitted their use under conditions where flammable or more toxic refrigerants would be hazardous to use. There is a "Freon" refrigerant for every application from home and industrial air conditioning to special low-temperature requirements. Some of the applications are outlined below.

"Freon-11", CCl_3F , boiling at 74.8°F (23.8°C), is widely used in centrifugal compressors for industrial and commercial air-conditioning systems and for industrial process water and brine cooling. Its low viscosity and freezing point have also led to its use as a low-temperature brine.

"Freon-12", CCl_2F_2 , boiling at -21.6°F (-29.8°C), is the most widely known and used of the "Freon" refrigerants. It is used principally in household and commercial refrigeration and air conditioning, for refrigerators, frozen food cabinets, ice cream cabinets, food locker plants, water coolers, room and window air-conditioning units and similar equipment. It is generally used in reciprocating compressors ranging in size from fractional to 800 horsepower and in rotary-type compressors in the smaller sizes. The use of centrifugal compression with "Freon-12" for large air-conditioning and process-cooling applications is increasing.

"Freon-13", CClF_3 , boiling at -114.6°F (-81.4°C), is used in low-temperature specialty applications using reciprocating compressors and generally in cascade with "Freon-12" or "Freon-22".

"Freon-22", CHClF_2 , boiling at -41.4°F (-40.8°C), is used in all types of household and commercial refrigeration and air-conditioning applications with reciprocating compressors. The outstanding thermodynamic properties of "Freon-22" permit the use of smaller equipment than is possible with similar refrigerants—making it especially attractive for uses where size is a problem.

"Freon-113", $\text{CCl}_2\text{F}-\text{CClF}_2$, boiling at 117.6°F (47.6°C), is used in commercial and industrial air conditioning and process water and brine cooling with centrifugal compression. It is especially useful in small tonnage applications.

"Freon-114", $\text{CClF}_2-\text{CClF}_2$, boiling at 38.4°F (3.6°C), is used in small refrigeration systems with rotary-type compressors and in large industrial process cooling and air-conditioning systems using multistage centrifugal compressors.

"Freon-115", $\text{CClF}_2-\text{CF}_3$, boiling at -37.7°F (-38.7°C), is an especially stable refrigerant offering a particularly low discharge temperature in reciprocating compressors. Its capacity exceeds that of "Freon-12"

by as much as 50 per cent in low-temperature systems and its potential applications include household refrigerators and automobile air conditioning.

"Freon-502" is an azeotropic mixture composed of 48.8 per cent "Freon-22" and 51.2 per cent "Freon-115", by weight, which boils at -50.1°F (-45.6°C). Because it permits achieving the capacity of "Freon-22" with discharge temperatures comparable to "Freon-12" in reciprocating compressors, it is finding new applications in low-temperature cabinets for display, storage and freezing of foodstuffs.

"Freon-13B1", CBrF_3 , boiling at -72°F (-57.8°C), offers higher capacity at low temperatures than any refrigerant currently available commercially. Specific applications are under development.

PROPELLENTS—The development of pressurized, self-propelled aerosol products using liquefied-gas propellents was centered around the "Freon" compounds. Their characteristic stability, nonflammability, low degree of toxicity and lack of odor provide a unique combination of properties especially desirable for the propelling force in this rapidly expanding industry.

The versatility of "Freon" propellents is almost unlimited. The right propellant for nearly every purpose can be tailor-made by selecting the right "Freon" compound or combination of compounds. Most aerosol formulations require a propellant which is a solution of two "Freon" compounds so that the right pressure, stability and solvent properties can be obtained. Each aerosol formulation must be examined individually to be sure that the right propellant is used.

The most commonly used propellant for nonfood aerosols is "Freon-12", either by itself or in combination with other "Freon" compounds. It has a fairly high vapor pressure and provides most of the propelling force in aerosol formulations.

"Freon-11" is used with "Freon-12" to reduce the pressure and increase the solubility of other materials without harming gaskets and liners.

"Freon-114" is used either alone or with "Freon-12"—principally in the cosmetic field. It is exceptionally stable, practically odorless, and causes no undesirable effect when applied to the skin.

The possibilities of pressurized food products have been increased by the recent introduction of "Freon" C-318 propellant. This tasteless, odorless compound has been accepted by the U. S. Food and Drug Administration as a food additive. Used alone or mixed with nitrous oxide, "Freon" C-318 gives added foam stability and improved appearance to food products such as dessert toppings. Other food formulations are under development.

"Freon" propellents give excellent results with all types of aerosol formulations—including space sprays, surface-coating sprays, foam products, nonemulsified aqueous products and powders.

The wide range of application of the aerosol idea is indicated by the following partial list of products on the market: air sanitizer, antifoam sprays, antiperspirant, antistatic sprays, burn preparations, colognes, deodorants, fire alarm devices, fire extinguishers, foot sprays, garbage can sprays, hair dressings, hand lotions, insecticides, insect repellents, mothproofers, paints, pet products, pharmaceuticals, plant growth stimulators, protective coatings, shampoos, shaving creams, shoe polishes, silver antitarnish sprays, artificial snows, sun tan sprays, water repellents, waxes, window cleaners.

For further information write for our bulletin "Package For Profit."

SOLVENTS—Some of the "Freon" compounds have unique properties for use as solvents and cleaning agents. Their nonflammable, nonexplosive, relatively nontoxic and stable properties offer advantages which are not found in other solvents. They exhibit a selective solvent action which permits their use for removing oil, grease and dirt from many objects without harm to metal or plastic parts. The high density and low surface tension of the "Freon" solvents make possible a "washing" action which adds to their effectiveness as cleaning agents.

These solvents have found wide application in ultrasonic cleaning, vapor degreasing, cold cleaning and combinations of the foregoing. Their high stability permits easy recovery for reuse time after time. As a result of their purity and selectivity, they are ideal for "white room" applications as well as a variety of industrial cleaning applications.

The "Freon" solvents form azeotropes with a number of other organic solvents. Solvent properties may be modified and the range of applications extended. Several such blends are commercially available.

More complete information on "Freon" solvents and azeotropes is available on request.

CHEMICAL INTERMEDIATES—Vinyl fluoride and vinylidene fluoride are commercially available monomers which can be copolymerized with a wide variety of other monomers to give plastics, elastomers and resinous products with unusual properties. Incorporated into polymers, these fluoromonomers provide an effective way of increasing resistance to: solvent and chemical attack—low and high temperatures—hydrolysis—discoloration—radiation. They can impart to a product the qualities of thermal and chemical stability—mechanical strength—toughness—flexibility—inertness.

Other partially fluorinated products such as difluoroethane and chlorodifluoroethane can be used as starting materials for the preparation of monomers and also in chemical reactions involving the introduction of fluorine atoms into other molecules.

More specific information on monomers and other fluorinated products is available on request.

POLYMERIC FOAM BLOWING AGENTS—Some of the "Freon" compounds are finding wide application as

blowing agents for urethane, epoxy, polyolefin and other types of polymeric foams. In some foams, the "Freon" compound, when added to the mix, vaporizes as a result of the exothermic polymerization reaction, thereby causing a cellular formation. In other cases, a hot, pressure melt of the polymer and the "Freon" compound is extruded through a die, with the simultaneous cooling and release of pressure resulting in a cellular formation.

Use of "Freon" blowing agents in the preparation of rigid foams offers many advantages. Their high molecular weight and their retention in the foam systems are especially important in imparting excellent insulation properties to the foam. Low-density foams can be produced with fine uniform cell structure which provides high strength and durability.

Polymeric foams blown with "Freon" blowing agents have found successful application in such diversified fields as industrial and appliance insulation, transportation (trucks, trailers, airplanes, boats and automobiles), building construction, packaging, furniture, bedding and clothing.

More complete information is available in our BA series of technical bulletins.

FIRE EXTINGUISHING AGENTS—Nearly all of the "Freon" products have some effectiveness as fire extinguishing agents and might be used for this purpose in an emergency. However, for most effective results, the presence of bromine in the molecule has been found necessary and many compounds have been examined for their extinguishing ability. The most satisfactory from the standpoint of high effectiveness, chemical and thermal stability and low toxicity is "Freon" FE 1301 (bromotrifluoromethane).

"Freon" FE 1301 is used in commercial aircraft for protection against in-flight engine fires and in portable Class B and C extinguishers for both the military and civilian markets.

More complete information on "Freon" fire extinguishing agents is available in "Freon" Technical Bulletin B-29.

DIELECTRIC FLUIDS—The "Freon" compounds have high dielectric strength in both liquid and vapor phases and are used as insulating liquids or vapors in many types of electric and electronic equipment. Good thermal stability and compatibility with most metals of construction enable them to be used in a wide variety of applications. Some of the higher boiling products are used as ebullient coolants while lower boiling members of the "Freon" series are used as vapor phase insulating gases. Some "Freon" products still in the development stage have unusually good dielectric and coolant properties. Further information can be obtained from the "Freon" Products Division.

OTHER USES—The unique combination of properties found in the "Freon" products has led to their application in other fields such as heat-transfer fluids, power fluids, etc.

PHYSICAL PROPERTIES CHART

Unless otherwise noted, data in the chart were developed by the Du Pont Company in its laboratories or under contract with outside laboratories.

Other References

1. "Freon-13" freezing point from Ruff and Keim, *z. anorg. allgem. Chem.* 201 245 (1931).
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3. Critical constants calculated according to Meissner and Redding, *Ind. Eng. Chem.* 34 521 (1942).
4. "Freon-116" data from Pace and Aston, *J. Am. Chem. Soc.* 70 566 (1948).
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6. "Freon-112" data from Hovorka and Geiger, *J. Am. Chem. Soc.* 55 4759 (1933).
7. Liquid thermal conductivity estimated by a general correlation method.
8. Data from Du Pont at one atmosphere, 0.1 inch gap and $\frac{1}{4}$ inch sphere-to-plane gap.
9. Vapor dielectric constants from Fuoss, *J. Am. Chem. Soc.* 60 1633 (1938).
10. "Freon-115" freezing point from Calfee, Fukuhara, Young and Bigelow, *J. Am. Chem. Soc.* 62 267 (1940).
11. Cleveland et al, *J. Mol. Spec.* 7 209 (1961).
12. Underwriters' Laboratories' Report. Copies are available from Du Pont on request.
13. Result based on preliminary toxicological data.

SHIPPING CONTAINERS

"Freon-11"	"Freon-12"	"Freon-13"	"Freon-13B1"	"Freon-22"	"Freon-113"	"Freon-114"
Capacity in Pounds						
100*	10	5	6	9	100*	10
200*	25	9	10	22	200*	25
650*	50	23	28	50	690*	150
2200	145	80	150	125	2200	2200
	2000		2000	1750		

*Nonreturnable drum.

For further information on shipping containers write for Bulletin B-3.

BULK SHIPMENT

Most of the "Freon" fluorocarbon compounds may also be shipped in single unit rail tank cars or motor cargo

tank trucks. Please write for details if you are interested in this method of shipment.

TECHNICAL SERVICE

The "Freon" Products Division of the Du Pont Company is the original manufacturer of organic fluorine compounds. Our more than 30 years' experience in the manufacture, handling and use of these com-

pounds is available to assist you in applying the "Freon" family of fluorinated compounds to your needs. If we can be of service to you please write or call one of the sales offices listed on the back cover.

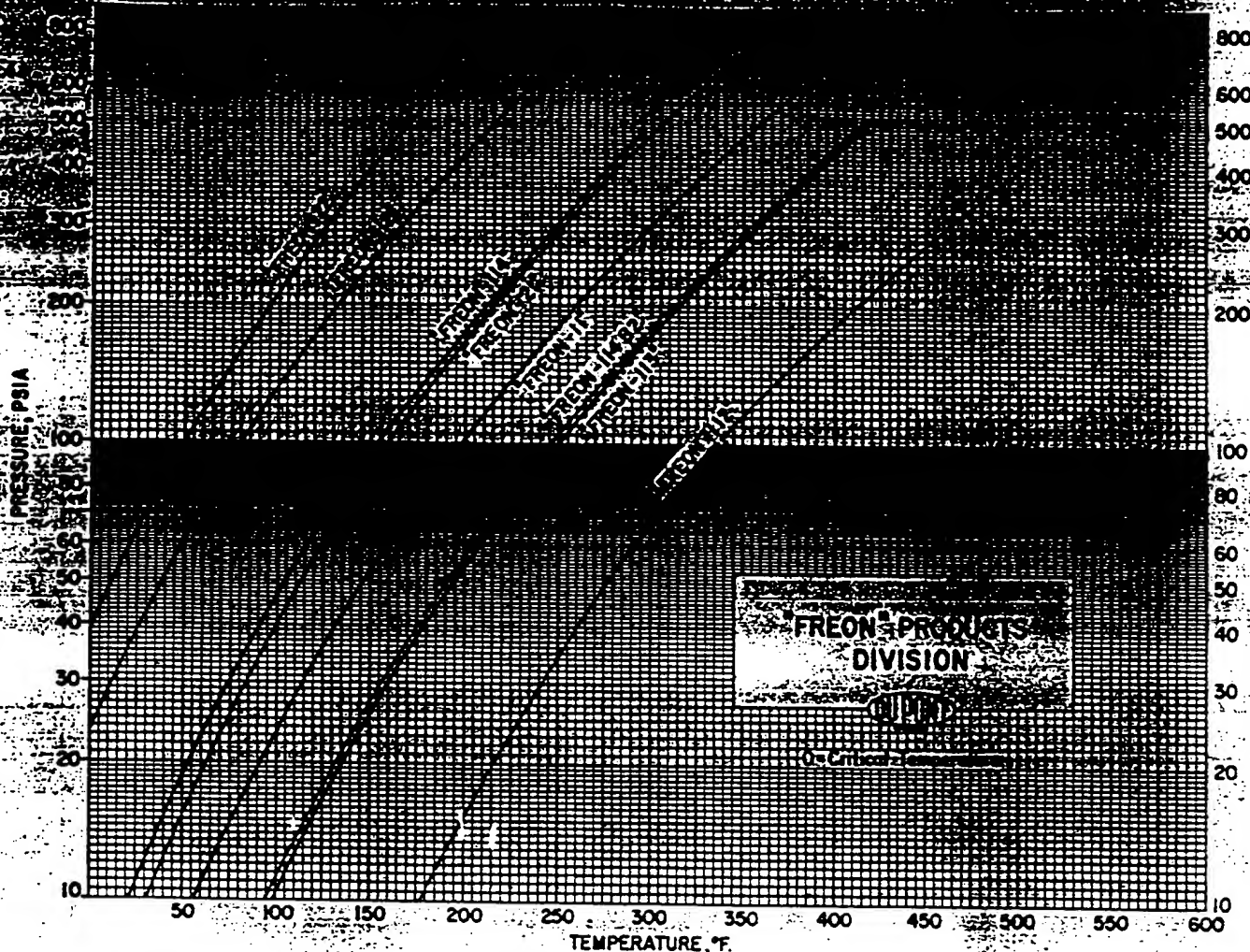
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PRESSURE-TEMPERATURE RELATIONSHIPS OF FREON PRODUCTS AT HIGH TEMPERATURES

C-22



FREON PRODUCTS
DIVISION

DUPONT

(See Critical Temperatures)

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